22/08(a)

The University of Sydney

CHEMISTRY 1A (ADVANCED) - CHEM1901

CHEMISTRY 1A (SPECIAL STUDIES PROGRAM) - CHEM1903

FIRST SEMESTER EXAMINATION

CONFIDENTIAL

JUNE 2003 **TIME ALLOWED: THREE HOURS**

GIVE THE FOLLOWING INFORMATION IN BLOCK LETTERS

FAMILY NAME		**SID NUMBER**	
OTHER NAMES		**TABLE NUMBER**	

INSTRUCTIONS TO CANDIDATES

- All questions are to be attempted. There are 19 pages of examinable material.
- Complete the written section of the examination paper in **INK.**
- Read each question carefully. Report the appropriate answer and show all relevant working in the space provided.
- The total score for this paper is 100. The possible score per page is shown in the adjacent tables.
- Each new short answer question begins with a •.
- Electronic calculators, including programmable calculators, may be used. Students are warned, however, that credit may not be given, even for a correct answer, where there is insufficient evidence of the working required to obtain the solution.
- Numerical values required for any question and a Periodic Table may be found on a separate data sheet.
- Pages 12, 16, 22 & 24 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-11	41	

Short answer section

Page	Marks			Marker
	Max	Gained		
13	6			
14	5			
15	8			
17	6			
18	4			
19	7			
20	8			
21	9			
23	6			
Total	59			

Marks

- Use the thermochemical data provided to calculate the heat of reaction of the following reaction: **2**

$$PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s)$$

Data: $P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(l)$ $\Delta H° = -1280$ kJ mol^{-1}

$P_4(s) + 10Cl_2(g) \rightarrow 4PCl_5(s)$ $\Delta H° = -1774$ kJ mol^{-1}

ANSWER:

- Identify one property of a molecule necessary for it to be considered a "greenhouse gas". **1**

- Write a balanced nuclear equation for the formation of $^{222}_{86}Rn$ through alpha particle emission. **1**

- Explain, in terms of the quantum theory of electrons, why the electronic energy is decreased by the delocalisation of the valence electrons in the metallic bond. **2**

Marks

- Explain why electrons in atoms occupy discrete energy levels rather than being able to possess any possible energy below that required for ionisation. **2**

- A certain pigment is found to have an electronic excitation energy of 4.97×10^{-19} J. What is the wavelength at which this molecule will absorb radiation? **3**

ANSWER:

What colour do you expect this pigment to be? Explain your answer.

Marks

- Complete the following table. 3

Molecule	<u>S</u>O_2	<u>P</u>F_3	<u>Xe</u>F_2
Number of non-bonding valence electron pairs about the underlined atom			
Number of valence electron pairs about the underlined atom involved in σ-bonding.			
Shape of molecule			

- 40.0 mL of 0.850 M HNO_3 is combined with 60.0 mL of 0.540 M NaOH in a calorimeter. The calorimeter heat capacity is 80.0 J K^{-1} and the heat capacity of the final solution is 426 J K^{-1}. The temperature was found to increase by 3.58 °C. Determine the molar heat of reaction for the process $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$. 3

ANSWER:

- Tritium, ^3_1H, in nuclear warheads decays with a half life of 12.26 years and must be replaced. What fraction of the tritium is lost in 5.0 years? 2

ANSWER:

Marks

- Consider the boiling points of the following hydrides: 3

compound	boiling point (K)
H_2O	373
HF	293
NH_3	240
CH_4	111

Explain the origin of the difference in boiling points between:

i) CH_4 and NH_3

ii) HF and NH_3

iii) H_2O and HF

- Which molecule in each of the following pairs has the greater dipole moment? Give reasons for your choice. 3

a) SO_2 or SO_3

b) SiF_4 or SF_4

c) H_2S or H_2Te

Marks

- The normal boiling point of chloroform is 61.7 °C and its enthalpy of vaporisation is 31.4 kJ mol^{-1}. Calculate the entropy of vaporisation for chloroform at 1 atm. **2**

Answer:

- Write balanced net ionic equations for the reactions that occur in each of the following cases. **2**

Dilute hydrochloric acid is added to solid sodium carbonate.

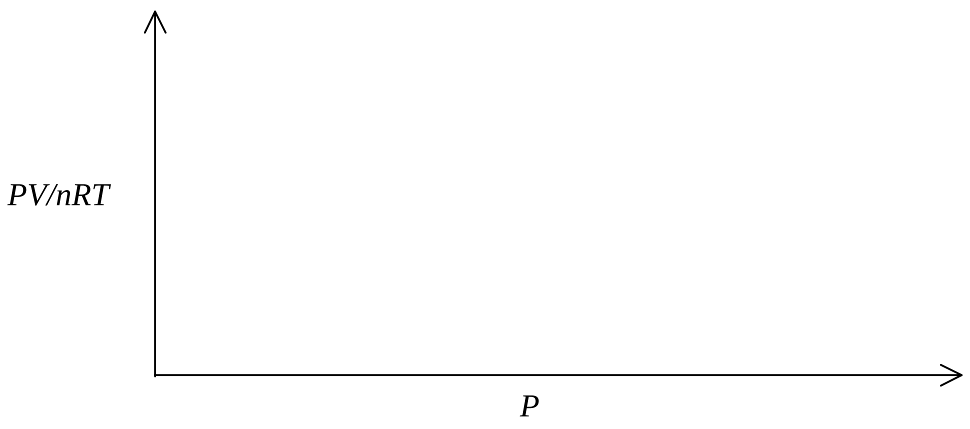
Excess water is added to solid potassium oxide.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks

- Find the volume of hydrogen gas collected over water when 1.00 g of zinc is dissolved in excess dilute hydrochloric acid at 27 ºC and 1.000 atm pressure. The vapour pressure of water at 27 ºC is 3.6 kPa. **3**

- Sketch to high pressure a plot of *PV/nRT* against pressure for: (a) an ideal gas, (b) H_2 gas and (c) CO_2 gas **2**



- In a diffusion experiment, an unknown gas diffused 2.646 times faster than nitrogen gas in the same apparatus under the same physical conditions. Calculate the molar mass of, and suggest an identity for, the unknown gas. **2**

Marks
8

- The decomposition of ozone to oxygen gas, $2O_3(g) \rightarrow 3O_2(g)$, is found to have the following rate law:

$$\text{Rate} = k[O_3]$$

Provide a mechanism for this reaction that is consistent with this rate law.

At –45 °C, the temperature of the ozone layer, and with an initial ozone concentration of 1.00×10^{-3} mol L^{-1} the rate of formation of O_2 is 1.05×10^{-7} mol L^{-1} s^{-1}. How long would it take for the O_3 concentration to drop to half of its initial concentration at this temperature?

One important mechanism for the destruction of ozone in the upper atmosphere is

$$O_3(g) + NO(g) \rightarrow NO_2(g) + O_2(g)$$
$$NO_2(g) + O(g) \rightarrow NO(g) + O_2(g)$$

Overall $\quad O_3(g) + O(g) \rightarrow 2O_2(g)$

Name the species that are the catalyst and the intermediate in this two-step reaction.

E_a for the catalysed reaction is 11.9 kJ mol^{-1} whereas E_a for the uncatalysed reaction is 14.0 kJ mol^{-1}. At – 45 ºC, what is the ratio of the rate constant for the catalysed reaction to that of the uncatalysed reaction? Assume that the frequency factor, A, is the same for each reaction.

Marks

- Calculate $[H^+]$, $[OH^-]$, $[H_2CO_3]$, $[HCO_3^-]$ and $[CO_3^{2-}]$ in a 0.0010 M carbonic acid solution. Carbonic acid (H_2CO_3) is a diprotic acid with $K_{a1} = 4.5 \times 10^{-7}$ M and $K_{a2} = 4.7 \times 10^{-11}$ M. **5**

$[H^+]$ =	$[OH^-]$ =	$[H_2CO_3]$ =
$[HCO_3^-]$ =	$[CO_3^{2-}]$ =	

- What volumes of 0.20 M solutions of HNO_2 and KNO_2 are required to make 1.0 L of a buffer solution of pH 3.00? (K_a for $HNO_2 = 4.0 \times 10^{-4}$ M) **3**

- The ionisation constant of water, K_w, at 37 °C is 2.42×10^{-14} M^2. Calculate the pH of a neutral solution at this temperature. **1**

pH =

Marks
6

- If wet silver carbonate is dried in a stream of hot air, the air must have a certain concentration level of carbon dioxide to prevent decomposition by the reaction

$$Ag_2CO_3(s) \rightleftharpoons Ag_2O(s) + CO_2(g)$$

The enthalpy change, $\Delta H°$, for this reaction is 79.14 kJ mol^{-1} in the temperature range of 25 to 125 °C. Given that the partial pressure of CO_2 in equilibrium with solid Ag_2CO_3 is 8.20×10^{-6} atm at 25 °C, calculate the partial pressure of CO_2 necessary to prevent decomposition of Ag_2CO_3 at 110 °C. Assume that $\Delta S°$ does not change over this temperature range.

Answer:

For the above reaction at equilibrium, describe what would happen to the equilibrium CO_2 pressure, the Gibbs free energy, and to the equilibrium constant if each of the following changes were made separately. Write *increased*, *decreased*, or *unchanged* in the table below.

CHANGE	equilibrium CO_2 pressure	ΔG	K_p
CO_2 gas is injected at constant volume			
The temperature is increased			

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Numerical Data

Physical constants

Planck constant = h = 6.626 × 10^{-34} J s

Speed of light in vacuum = c_o = 2.998 × 10^{8} m s^{-1}

Avogadro constant = N_A = 6.022 × 10^{23} mol^{-1}

Faraday constant = F = 96485 C mol^{-1}

Ideal gas constant = R = 8.314 J K^{-1} mol^{-1}

= 0.08206 L atm K^{-1} mol^{-1}

Volume of 1 mol of ideal gas at 1 atm, 0 °C = 22.4 L

Volume of 1 mol of ideal gas at 1 atm, 25 °C = 24.5 L

Conversion factors

0 °C = 273 K

1 atm = 101.3 kPa = 760.0 mmHg

1 nm = 10^{-9} m

1 MHz = 10^{6} Hz = 10^{6} s^{-1}

1 L = 10^{-3} m^{3}

A periodic table is printed on the other side of this data sheet.
Atomic weights are included in the periodic table.

PERIODIC TABLE OF THE ELEMENTS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 HYDROGEN **H** 1.008																	2 HELIUM **He** 4.003
3 LITHIUM **Li** 6.941	4 BERYLLIUM **Be** 9.012											5 BORON **B** 10.81	6 CARBON **C** 12.01	7 NITROGEN **N** 14.01	8 OXYGEN **O** 16.00	9 FLUORINE **F** 19.00	10 NEON **Ne** 20.18
11 SODIUM **Na** 22.99	12 MAGNESIUM **Mg** 24.31											13 ALUMINIUM **Al** 26.98	14 SILICON **Si** 28.09	15 PHOSPHORUS **P** 30.97	16 SULFUR **S** 32.07	17 CHLORINE **Cl** 35.45	18 ARGON **Ar** 39.95
19 POTASSIUM **K** 39.10	20 CALCIUM **Ca** 40.08	21 SCANDIUM **Sc** 44.96	22 TITANIUM **Ti** 47.88	23 VANADIUM **V** 50.94	24 CHROMIUM **Cr** 52.00	25 MANGANESE **Mn** 54.94	26 IRON **Fe** 55.85	27 COBALT **Co** 58.93	28 NICKEL **Ni** 58.69	29 COPPER **Cu** 63.55	30 ZINC **Zn** 65.39	31 GALLIUM **Ga** 69.72	32 GERMANIUM **Ge** 72.59	33 ARSENIC **As** 74.92	34 SELENIUM **Se** 78.96	35 BROMINE **Br** 79.90	36 KRYPTON **Kr** 83.80
37 RUBIDIUM **Rb** 85.47	38 STRONTIUM **Sr** 87.62	39 YTTRIUM **Y** 88.91	40 ZIRCONIUM **Zr** 91.22	41 NIOBIUM **Nb** 92.91	42 MOLYBDENUM **Mo** 95.94	43 TECHNETIUM **Tc** [98.91]	44 RUTHENIUM **Ru** 101.07	45 RHODIUM **Rh** 102.91	46 PALLADIUM **Pd** 106.4	47 SILVER **Ag** 107.87	48 CADMIUM **Cd** 112.40	49 INDIUM **In** 114.82	50 TIN **Sn** 118.69	51 ANTIMONY **Sb** 121.75	52 TELLURIUM **Te** 127.60	53 IODINE **I** 126.90	54 XENON **Xe** 131.30
55 CAESIUM **Cs** 132.91	56 BARIUM **Ba** 137.34	57-71	72 HAFNIUM **Hf** 178.49	73 TANTALUM **Ta** 180.95	74 TUNGSTEN **W** 183.85	75 RHENIUM **Re** 186.2	76 OSMIUM **Os** 190.2	77 IRIDIUM **Ir** 192.22	78 PLATINUM **Pt** 195.09	79 GOLD **Au** 196.97	80 MERCURY **Hg** 200.59	81 THALLIUM **Tl** 204.37	82 LEAD **Pb** 207.2	83 BISMUTH **Bi** 208.98	84 POLONIUM **Po** [210.0]	85 ASTATINE **At** [210.0]	86 RADON **Rn** [222.0]
87 FRANCIUM **Fr** [223.0]	88 RADIUM **Ra** [226.0]	89-103	104 RUTHERFORDIUM **Rf** [261]	105 DUBNIUM **Db** [262]	106 SEABORGIUM **Sg** [266]	107 BOHRIUM **Bh** [262]	108 HASSIUM **Hs** [265]	109 MEITNERIUM **Mt** [266]									

LANTHANIDES	57 LANTHANUM **La** 138.91	58 CERIUM **Ce** 140.12	59 PRASEODYMIUM **Pr** 140.91	60 NEODYMIUM **Nd** 144.24	61 PROMETHIUM **Pm** [144.9]	62 SAMARIUM **Sm** 150.4	63 EUROPIUM **Eu** 151.96	64 GADOLINIUM **Gd** 157.25	65 TERBIUM **Tb** 158.93	66 DYSPROSIUM **Dy** 162.50	67 HOLMIUM **Ho** 164.93	68 ERBIUM **Er** 167.26	69 THULIUM **Tm** 168.93	70 YTTERBIUM **Yb** 173.04	71 LUTETIUM **Lu** 174.97
ACTINIDES	89 ACTINIUM **Ac** [227.0]	90 THORIUM **Th** 232.04	91 PROTACTINIUM **Pa** [231.0]	92 URANIUM **U** 238.03	93 NEPTUNIUM **Np** [237.0]	94 PLUTONIUM **Pu** [239.1]	95 AMERICIUM **Am** [243.1]	96 CURIUM **Cm** [247.1]	97 BERKELLIUM **Bk** [247.1]	98 CALIFORNIUM **Cf** [252.1]	99 EINSTEINIUM **Es** [252.1]	100 FERMIUM **Fm** [257.1]	101 MENDELEVIUM **Md** [256.1]	102 NOBELIUM **No** [259.1]	103 LAWRENCIUM **Lr** [260.1]